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CONSEQUENCES OF RECYCLED CARBON IN CARBONATITES

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ABSTRACT

Formerly, carbonatites were thought to be results of the mantle's purging itself of "juvenile" carbon. However, evidence has been accumulating that carbon from the crust is recycled deep into the mantle by subduction. This non-juvenile carbon may nourish carbonatitic magmas. The process by which carbon in the mantle may eventually be incorporated into carbonatite in the crust is probably a circuitous one, involving transport in a variety of phases before accumulation in diverse sources of carbonatitic magma. With time, these sources have become more varied and more radiogenic. During its migration, carbonate liquid acts as an efficient sequestering agent in the mantle, gathering a distinctive retinue of trace elements, especially Sr, Nb, Ba, the light rare-earth elements, Pb, Th, and U. Elements that are strongly depleted in carbonatites are Si, Al, Mg, Cr, and Ni. Partition coefficients for carbonate liquid/minerals yield calculated enrichments that do not agree with those observed unless there are repeated episodes of interaction between carbonate liquid and progressively enriched mantle. Carbonate-rich liquid can only survive its upward passage if the rock through which it flows has already lost most of its capacity to react with carbonate liquid. Such "path clearing" requires the aborted ascent of precursor batches of carbonatitic magma. Ultramafic xenoliths from many localities have trace-element and isotopic enrichment and depletion patterns attributed to metasomatic reactions of lithospheric mantle with carbonate-rich liquids. These carbonate-metasomatized xenoliths indicate repeated invasion of the lithosphere by carbon-bearing liquids or fluids. This in turn implies that the rarity of carbonatitic magma in the upper crust is caused by barriers to its ascent, not by a shortage of source material.

Keywords: carbonatite, lithospheric mantle, metasomatism, carbon cycle.

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On considérait couramment le magmatisme carbonatitique comme manifestation d'une purgation du manteau en carbone "juvénile". Toutefois, il devient de plus en plus évident que le carbone d'origine crustale est recyclé dans le manteau par subduction. Ce carbone d'origine non juvénile peut ré-apparaître sous forme de magma carbonatitique. Le cheminement du carbone recyclé en manifestation carbonatitique dans la croûte serait de toute évidence tortueux, impliquant un tranfert dans une variété de phases minérales avant l'incorporation dans un magma carbonatitique. Avec le temps, les sources sont devenues plus variées et plus radiogéniques. Au cours de sa migration, le magma carbonaté agit comme solvent important dans le manteau, et accumule ainsi une suite distinctive d'éléments traces, particulièrement Sr, Nb, Ba, les terres rares légères, Pb, Th et U. Par contre, les éléments Si, Al, Mg, Cr et Ni sont fortement appauvris dans les carbonatites. Les coefficients de partage entre liquide carbonatitique et minéraux semblent prédire des enrichissements qui ne concordent pas avec les enrichissements observés, à moins qu'il y ait eu des épisodes répétés d'interaction entre liquide carbonaté et manteau progressivement enrichi. Un liquide carbonaté ne pourrait subsister au cours de sa montée que si les roches le long des parois des filons nourriciers ont perdu leur capacité de réagir avec ce liquide. Une telle préparation des chenaux nourriciers implique la présence de venues précoces avortées de magma carbonatitique. Des xénolithes ultramafiques à plusieurs endroits témoignent, par un schéma d'enrichissements et d'appauvrissement en éléments traces et en isotopes, de réactions métasomatiques dans le manteau lithosphérique impliquant un liquide carbonaté. La métasomatose des xénolithes indiquerait l'invasion répétée de la lithosphère par des venues de liquide ou de fluide contenant du carbone. La rareté de manifestations carbonatitiques dans la croûte supérieure serait due surtout aux entraves à la mobilité du magma au cours de son ascension, plutôt qu'à une pénurie de matériau approprié à la source.

(Traduit par la Rédaction)

Mots-clés: carbonatite, manteau lithosphérique, métasomatose, cycle du carbone.

RECYCLING OF CARBON INTO THE MANTLE

Evidence for return of carbon to the mantle from the crust comes from very high-pressure (coesite- and diamond-bearing) assemblages in metasedimentary rocks, from experiments at pressures, temperatures, and compositions appropriate to subducting carbonate-bearing oceanic crust, and from mass-balance and isotopic constraints. Schreyer (1995) and Harley & Carswell (1995) reviewed the occurrences of very high-pressure metasedimentary carbonate rocks, exhumed from depths of 100 to 130 km. Yaxley & Green (1994) showed experimentally that calcite and dolomite can survive in subducting oceanic crust as refractory phases in eclogite, even in the presence of silicate melt. Staudigel *et al.* (1989) calculated that subduction of altered oceanic crust containing carbonate veins is an efficient way to return carbon to the mantle. Varekamp *et al.* (1992) found that gases released at volcanic arcs have higher values of $C/^3He$ than do those released along mid-ocean ridges, and concluded that more than 80% of CO_2 exhaled by arc volcanoes was recycled from subducted crust. Zhang & Zindler (1993) used the ratio $C/^3He$ in gases released at mid-ocean ridges to estimate the flux of carbon from the mantle, and found that this rate could provide all of the carbon in the Earth's atmosphere, hydrosphere, and crust in 3 b.y. Such rapid degassing suggests reflux of carbon into the mantle. Their modeling indicates that the total amount of carbon in the crust has decreased since Precambrian time, a conclusion also reached by Koster van Groos (1988).

These independent lines of evidence show that a substantial proportion of the carbon in carbonatites could be recycled. A suggestion that "juvenile" carbon be incorporated in the definition of carbonatite (Barker 1989) is therefore unduly restrictive. The aim of this paper is to examine the consequences of recycled, as contrasted to juvenile, carbon for the generation and distribution of carbonatites. After consideration of the mantle phases that contain carbon, the compositions of carbonate-rich liquids and their metasomatizing effects are summarized, followed by distribution of carbonatites through space and geological time, and finally, the factors that inhibit the ascent of carbonatite magmas and thus cause their rarity in the crust.

CARBON-BEARING PHASES IN THE MANTLE

Experimental studies show that dolomite and magnesite can be stable in the deep mantle (Dalton & Wood 1993b, Biellmann *et al.* 1993, Redfern *et al.* 1993). Carbonate minerals, however, are rare in ultramafic mantle-derived xenoliths (Berg 1986, Smith 1979, 1987). Decompression during ascent probably destroys carbonates in most xenoliths (Canil 1990), but some relatively coarse-grained carbonates have survived (Ionov *et al.* 1993). Carbon can also be present in the mantle as the CO_3^{2-} component in magma; as CO_2, CO, and CH_4 components in a fluid phase, as the solid phases graphite, diamond, and SiC (Mathez *et al.* 1995), in intergranular films of amorphous carbonaceous material, and in tetrahedral sites of silicates and oxides. Wang *et al.* (1994) provided a brief review of most of these alternatives.

Phase relations in carbonate-bearing peridotite have been investigated most recently by Green & Wallace (1988), Falloon & Green (1989, 1990), Canil & Scarfe (1990), Wyllie *et al.* (1990), Ryabchikov *et al.* (1991), Thibault *et al.* (1992), Edgar (1993), and Sweeney (1994). Dolomitic liquid coexists with peridotite at 20 to 50 kbar and 930 to 1200°C (Sweeney 1994). As discussed by Ryabchikov *et al.* (1991), the solidus for apatite-bearing carbonated lherzolite + H_2O is close to the range of stable continental geotherms at 30 kbar. Consequently, small volumes of carbonate-rich melt may form at many places and times in subcontinental mantle. However, liquid dominated by carbonate differs from silicate liquid in important ways in addition to composition. The essential component, CO_3^{2-}, does not exist at all times and places in the source rock and may be formed by oxidation of elemental carbon, carbon monoxide, or methane. Generation of carbonate-rich liquid, in contrast to silicate liquid, requires a range of oxygen fugacity that may not everywhere be attained in the mantle (Dalton & Wood 1995). Furthermore, carbonate-rich liquid can react with silicate wallrock in such a manner that the liquid decomposes by evolution of CO_2 as a component of a fluid phase; see below, under "Halting the rise of carbonatite magma". As a result of these complexities, recycled carbon between its subduction and its return to the crust may go through several phases.

COMPOSITIONS OF CARBONATITE

Table 1 compares the average calciocarbonatite of Woolley & Kempe (1989) with estimated compositions of pyrolite mantle (McDonough & Sun 1995) and continental crust (Wedepohl 1995). The relative enrichments and depletions are given in tabular form, rather than the familiar spidergrams, so that a more complete list of elements can be presented without assuming a particular order of incompatibility. The comparison is weakened by uncertainties in the carbonatite average; for example, the estimates for Sm, Eu, and Dy are based on only two analyses each. Although dolomitic magma can be primary (Bailey 1993a, Sweeney 1994), the averages for magnesiocarbonatite and ferrocarbonatite reported by Woolley & Kempe (1989) are based on fewer analyses than for calciocarbonatite, so the latter were taken as representative of carbonate-rich melts. Furthermore, many Mg- and Fe-rich carbonatites appear to be of secondary, subsolidus, origin (Barker 1993).

Partition coefficients for carbonate liquid *versus* the

TABLE 1. CARBONATITE: ENRICHMENTS AND DEPLETIONS

	carbonatite[1]/pyrolite[2]	carbonatite[1]/continental crust[3]
Si	0.06	0.04
Ti	0.75	0.22
Al	0.24	0.07
Fe	0.38	0.55
Mn	3.85	5.62
Mg	0.05	0.50
Ca	13.9	9.12
Na	0.81	0.09
K	8.99	0.10
P	102	12.1
C	836	50.3
F	116	5.52
Cl	47.1	1.69
S	30.4	10.9
Be	353	10.0
Sc	0.43	0.44
V	0.98	0.82
Cr	0.005	0.10
Co	0.10	0.46
Ni	0.009	0.32
Cu	0.80	0.96
Zn	3.42	2.89
Rb	23.3	0.18
Sr	366	21.9
Y	27.6	4.96
Zr	17.6	0.91
Nb	1830	63.4
Ba	462	5.22
La	938	20.3
Ce	1007	28.1
Nd	706	32.7
Sm	320	24.5
Eu	253	30.0
Dy	50	8.95
Yb	11.3	2.50
Pb	373	3.78
Th	654	6.12
U	429	5.12

1 Average calciocarbonatite of Woolley & Kempe (1989).
2 Silicate Earth – Pyrolite of McDonough & Sun (1995, p. 238).
3 Continental crust of Wedepohl (1995, p. 1220).

TABLE 2. EXPERIMENTAL PARTITION COEFFICIENTS (CARBONATE LIQUID/MINERAL)

	ol	opx	cpx	grt	amp	phl
K	50 g	50 g	50 g	>7 b 111 g	0.4 b	0.3 g
Ti	>20 g	7.7 g	0.7 f 8.3 g	0.6 b 1.0 g	0.3 b	0.5 g
Rb	..	..	250 a	>250 b	3.6 a 2.4 b	0.25 g
Sr	5000 c 50 g	19 g	33 a 23 c 12.5 f 3.8 g	333 a 590 b 125 g	25 a 14 b	18 g
Y	>33 g	5.6 g	5 a 3.3 f 3.7 g	0.7 a 0.3 b 0.7 g	5 a 5 b	>25 g
Zr	28 g	5.9 g	3 a 2.1 f 3.4 g	1.9 a 0.25 b 1.25 g	4 a 1.25 b	20 g
Nb	29 g	>100 g	100 a 217 e	333 a 83 b	17 a 6 b	11 g
Ba	..	>20 g	167 a 2130 c 2630 e 14.3 f	333 a >50 b	100 a 11 b	1 g
Ce	7–50 d 50 g	>20 g	6 c 4–11 d 43 e 11.1 f 4.5 g	59 b	21 b	..

Sources: a Green *et al.* (1992), 25 kbar, 1000°C; b Sweeney *et al.* (1992), 27 kbar, 1000°C; c Brenan & Watson (1991), 15 kbar, 1150°C; d Ryabchikov *et al.* (1993), 20 kbar, 950°C; e Jones *et al.* (1995), 55 kbar, 1200°C; f Klemme *et al.* (1995), 20–22 kbar, 1050–1100°C; g Sweeney *et al.* (1995), 18–46 kbar, 1100–1250°C. Mineral symbols: ol olivine, opx orthopyroxene, cpx clinopyroxene, grt garnet, amp amphibole, phl phlogopite.

minerals encountered in peridotite have been experimentally measured by Brenan & Watson (1991), Green *et al.* (1992), Ryabchikov *et al.* (1993), Sweeney *et al.* (1992, 1995), Jones *et al.* (1995), and Klemme *et al.* (1995). Data on partition coefficients from experiments at 15 to 55 kbar and 950 to 1250°C are summarized in Table 2. Table 3 includes these results and attempts to fill out the data set for Rb in olivine and orthopyroxene, Ba in olivine, and Ce in phlogopite, using mineral/mineral partition coefficients for phases in equilibrium with basaltic liquid and the equation $D^{\text{carbonate liquid/mineral A}} = D^{\text{mineral B/mineral A}} \times D^{\text{carbonate liquid/mineral B}}$. The mineral/mineral partition coefficients are all taken from data in Green (1994) for internal consistency. Bulk partition-coefficients were calculated for carbonate liquid equilibrated with lherzolite containing 60% olivine, 20% orthopyroxene, 10% clinopyroxene, 7% garnet, 2% amphibole, and 1% phlogopite, with the assumption that all these phases persist in the solid assemblage.

For Sr, Nb, Ba, and Ce, the "observed" enrichments (average carbonatite/pyrolite, Table 1) are at least 20 times those predicted for 1% melting in Table 3. Because accessory phases were ignored in the calculations in Table 3, the bulk partition-coefficients for lherzolite/carbonate liquid are minimum values, and the predicted enrichments are maxima. One single-stage equilibration of average lherzolite with 1% carbonate liquid will not produce the large "observed" enrichments, and repeated fertilization of lherzolite through multiple encounters with carbonate liquid is needed.

Although carbonate liquid is efficient in scavenging and sequestering some trace elements, it is eclectic, and some carbonatites show little enrichment in these same

TABLE 3. CALCULATED PARTITION–COEFFICIENTS FOR LHERZOLITE/CARBONATE LIQUID

	ol	opx	cpx	grt	amp	phl	Bulk D^1	Predicted[2]
K	**0.02**	**0.02**	**0.02**	**0.009**	**2.5**	**3.3**	0.10	9
Ti	**0.05**	**0.13**	**0.12**	**1**	**3.3**	**2**	0.22	4
Rb	0.0008	0.004	**0.004**	**0.004**	**0.42**	**4.0**	0.05	17
Sr	**0.02**	**0.05**	**0.26**	**0.008**	**0.07**	**0.06**	0.05	17
Y	**0.03**	**0.18**	**0.27**	**1.43**	**0.2**	**0.04**	0.19	5
Zr	**0.04**	**0.17**	**0.29**	**0.8**	**0.8**	**0.05**	0.16	6
Nb	**0.03**	**0.01**	**0.01**	**0.01**	**0.17**	**0.09**	0.03	25
Ba	0.03	**0.05**	**0.07**	**0.02**	**0.09**	**1**	0.05	17
Ce	**0.02**	**0.05**	**0.22**	**0.02**	**0.05**	0.22	0.05	17

1 For lherzolite containing 60% olivine, 20% orthopyroxene, 10% clinopyroxene, 7% garnet, 2% amphibole, 1% phlogopite. 2 Concentration in carbonate liquid/concentration in lherzolite, calculated for 1% carbonate liquid equilibrated with lherzolite. K_d values in boldface are reciprocals of experimental data from Table 2; others were calculated as described in the text. Mineral symbols: ol olivine, opx orthopyroxene, cpx clinopyroxene, grt garnet, amp amphibole, phl phlogopite.

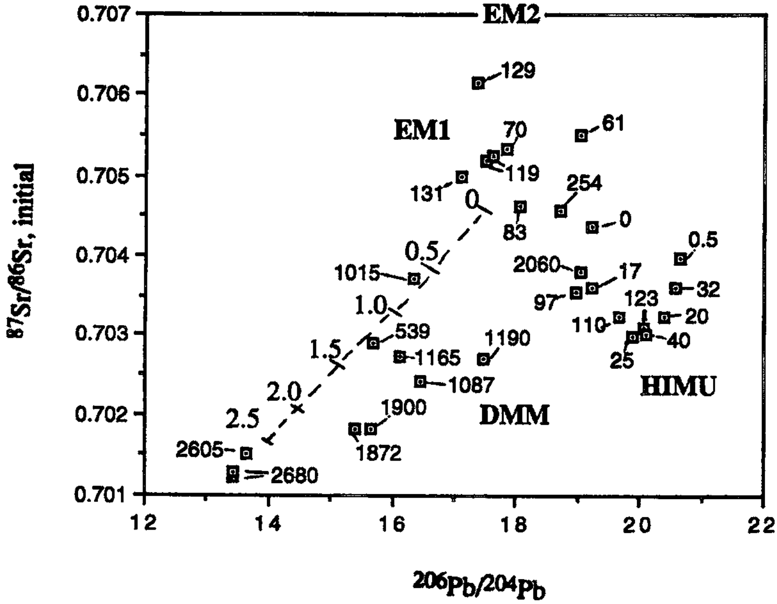

FIG. 1. Minimum reported initial $^{87}Sr/^{86}Sr$ *versus* minimum initial $^{206}Pb/^{204}Pb$ for carbonatites, compared with the mantle-source end-member components of Zindler & Hart (1986) and Hart (1988). DMM: depleted MORB-source mantle, HIMU: high U/Pb mantle, EM1: enriched mantle 1, EM2: enriched mantle 2. Bulk-earth evolution curve of Kwon *et al.* (1989, Fig. 14.8) is labeled in Ga. Numbers beside data points are ages (Ma). Data for Figures 1 and 2 are in the Appendix.

elements (for example, Nb is not enriched at Mountain Pass, California or in many African and Canadian carbonatites: Bell & Dawson 1995, Paslick *et al.* 1995). The large scatter in isotopic ratios as well as in trace-element concentrations reflects the variation in sources from which the carbonate-rich liquid drew its components. Figure 1, a plot of initial $^{87}Sr/^{86}Sr$ *versus* $^{206}Pb/^{204}Pb$, relates carbonatites to the mantle-source end members of Zindler & Hart (1986) and Hart (1988). These sources are best viewed as abstractions that refer to conditions, rather than as discrete volumes of mantle. Tilton & Bell (1994) showed that carbonatites younger than 200 Ma fall in this plot in an array between EM1 and HIMU end members, and those carbonatites that are older than 2.0 Ga plot in a tight cluster that indicates a much more depleted source. Figure 1 of this paper adds carbonatites of intermediate ages, and shows trends of increasing diversity and more highly radiogenic sources (with respect to Sr and Pb) through time. Phalaborwa (2060 Ma) and Fen (539 Ma) are strongly anomalous data-points on this trend; they indicate that radiogenic and depleted sources were locally available in Archean and in Paleozoic time, respectively.

The compilation of data on which Figures 1 and 2 are based is an Appendix to this paper. This appendix lists minimum reported ages, $^{87}Sr/^{86}Sr$ initial values, and $^{206}Pb/^{204}Pb$ values for 88 occurrences of carbonatite, and 53 source references. Neodymium isotopic data are not included because of the difficulty in ascertaining, from many of the publications, the normalization used for initial ratios and ε_{Nd}.

If some carbon in carbonatites is non-juvenile, its recycled nature should be shown by the $^{13}C/^{12}C$ isotopic ratio. This ratio, as expressed by $\delta^{13}C‰$ relative to PDB, ranges from –8 to –2 in carbonatites (Deines 1989), from –2 to +4 in marine sedimentary carbonates, and from –30 to –10 in organic (reduced) carbon (Faure 1986). Samples of diamond generally range from –8 to –2, but those in eclogite are from –34 to +4 (Pearson *et al.* 1994); graphite in peridotite and eclogite ranges from –20.3 to –2.8 (Pearson *et al.* 1994), and SiC is –29 to –22 (Mathez *et al.* 1995). CO_2-rich fluid inclusions in olivine from mid-ocean ridge and oceanic island basalts are –15 to –5 (Mattey *et al.* 1994).

The observed range in $\delta^{13}C$ of carbonatites does not overlap values of either marine carbonate or organic carbon. Taken at face value, this would indicate that recycled carbon does not contribute to carbonatites, unless it is the appropriate mixture of marine carbonate and organic carbon. Deines (1989, p. 327) has pointed out that because carbon is a major element in carbonatites but a trace element in the mantle, it must be extracted from large source-volumes and thus homogenized, converging on a relatively narrow range of $\delta^{13}C$ between those of sedimentary carbonate and reduced carbon.

Fractionation data are sparse at the pertinent temperatures and pressures, but Mattey *et al.* (1990) have measured carbon isotope fractionation at 1200 to 1400°C and 5 to 30 kbar; for CO_2 vapor equilibrated with either silicate or carbonate liquid, the vapor has the higher $\delta^{13}C$ by 2 to 2.4‰, and this fractionation appears to be independent of pressure and temperature over the ranges investigated. Between immiscible silicate and carbonate liquids, there is apparently no fractionation of carbon isotopes. Other experiments at mantle conditions are lacking, but fractionation factors at 600°C (Faure 1986, p. 500) should provide maximum values for fractionation at higher temperatures. CO_2 vapor equilibrated with methane, diamond, and calcite at 600°C has the higher (more positive) $\delta^{13}C$ values by 9, 7, and 2.5‰, respectively; graphite equilibrated with calcite and with diamond has the lower values by 5 and 0.5‰, respectively. These estimates allow little change in $\delta^{13}C$ values by single-stage processes, but multiple steps in the progression from subducted crust to solidified carbonatite may account for the observed variations. The $\delta^{13}C$ data thus support trace-element enrichments in indicating a multistage process to generate carbonatitic magma.

CARBONATITIC MAGMA AS A METASOMATIZING AGENT

Many ultramafic xenoliths from lithospheric mantle show textures and mineral assemblages that indicate modification of the original rock before the xenoliths were entrained in the magma that brought them to the surface. New minerals include clinopyroxene, spinel, phlogopite, amphibole and, rarely, apatite. Some of these xenoliths are enriched in light rare-earth elements, Ba, Rb, Sr, Pb, U, and Th, and are relatively depleted in Ti, Nb, Ta, Zr, and Hf (Meen *et al.* 1989, Dautria *et al.* 1992, Ionov *et al.* 1993, Hauri *et al.* 1993, Rudnick *et al.* 1993). These changes are generally attributed to interaction of lithospheric mantle with a carbonatitic magma. Roden *et al.* (1994) and Sweeney *et al.* (1995) summarized the criteria for carbonate metasomatism of mantle sources. Silicate liquids and hydrous or CO_2-rich fluids are considered less likely to produce the characteristic enrichments and depletions because they cannot dissolve sufficient amounts of the transported elements (Schneider & Eggler 1986, Watson *et al.* 1990) and have too large dihedral wetting angles to permeate ultramafic rock of the mantle (Watson & Brenan 1987). Carbonate liquid, on the other hand, has liquid/mineral partition coefficients, solidus relations, and physical properties that make it a likely agent of some mantle metasomatism (Green & Wallace 1988, Meen *et al.* 1989, Watson *et al.* 1990, Green *et al.* 1992, Ryabchikov *et al.* 1993, Baker & Wyllie 1992, Sweeney *et al.* 1992, 1995, Brenan & Watson 1991, Minarik & Watson 1995).

On comparing normal lherzolite of the lithospheric mantle with that modified by carbonatite-induced metasomatism, the latter has higher values for Ca/Al, Na/Ca, Ca/Sc, Ba/Rb, Ba/Nb, Nb/Ta, Sr/Ta, La/Ta, and Sr/Sm, lower values for Ti/Sr, Ti/Eu, and Zr/Y (Green *et al.* 1992, Rudnick *et al.* 1993, Sweeney *et al.* 1995), and lower Hf/Sm (Dupuy *et al.* 1992). Whether La/Nb increases or decreases is uncertain (Ionov *et al.* 1993, Rudnick *et al.* 1993). Hauri *et al.* (1993) also described metasomatized peridotite xenoliths from Samoa and the Austral Islands in which Pb is more highly radiogenic than Sr, and Sr more so than Nd. They attribute the metasomatism to carbonate-rich melts from recycled crust.

Pearson *et al.* (1994) have shown that graphite in xenoliths of peridotite, pyroxenite, and eclogite grew within its P–T stability field (*i.e.*, not metastably) and below solidus conditions. The carbon has $\delta^{13}C$ values that are the same as those of CO_2 in fluid inclusions in olivine phenocrysts in mid-ocean-ridge and oceanic-island basalts, and therefore are deduced by Pearson *et al.* to have come from below the lithosphere. These graphite-bearing xenoliths are rare, and appear to be derived only from lithosphere under Archean cratons. Pearson *et al.* (1994) concluded that the samples of graphite-bearing peridotite are not subducted oceanic lithosphere (because they lack the trace-element depletions expected in oceanic lithospheric mantle), and that the carbon was not expelled from subducting oceanic crust (because no carbon-bearing xenoliths have been found that were derived from mantle wedges overlying subduction zones). McInnes & Cameron (1994), however, have described carbonate-bearing ultramafic xenoliths from such a wedge, in Papua New Guinea.

The flow of magma in lithospheric mantle is much more likely to be controlled by fractures (Spera 1987, Wilshire & Kirby 1989, Nielson & Wilshire 1993), rather than by percolation through a porous medium, except within a few tens of centimeters of fractures. Metasomatism of the conduit walls protects later liquid that flows through the same fracture from reacting with the wallrock, so that later liquid can travel farther before being stalled by reaction (Meen 1987).

The wide geographic dispersal of these xenoliths of altered rock suggests that carbonate-rich liquid has been more common in the upper mantle than the sparse distribution of carbonatites in the upper crust would suggest. According to the testimony of these samples, carbonatitic magma, ascending through lithospheric mantle, commonly is trapped in fractures before it can invade oceanic or continental crust. These constitute veined sources like those invoked by Foley (1992) to yield ultrapotassic magmas. By analogy, carbonatitic magma could be produced by melting of carbonate-rich veins and their variably metasomatized wallrocks.

CARBONATITE MAGMATISM THROUGH TIME AND SPACE

Through geological time, the isotope ratios $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ in carbonatite become increasingly diverse and more radiogenic (Figs. 1, 2), as pointed out by Nelson *et al.* (1988), and Tilton & Bell (1994). Carbonatites are enriched in Sr, Nd, and Pb relative to crust (Table 1), and isotope ratios involving these elements in carbonatites are therefore relatively insensitive to crustal contamination; the isotopic ratios must reflect those of mantle sources. The general change through time in strontium, neodymium, and lead isotopic ratios of carbonatites toward more radiogenic values is well explained by storage of these incompatible elements in the lithosphere (Meen 1987,

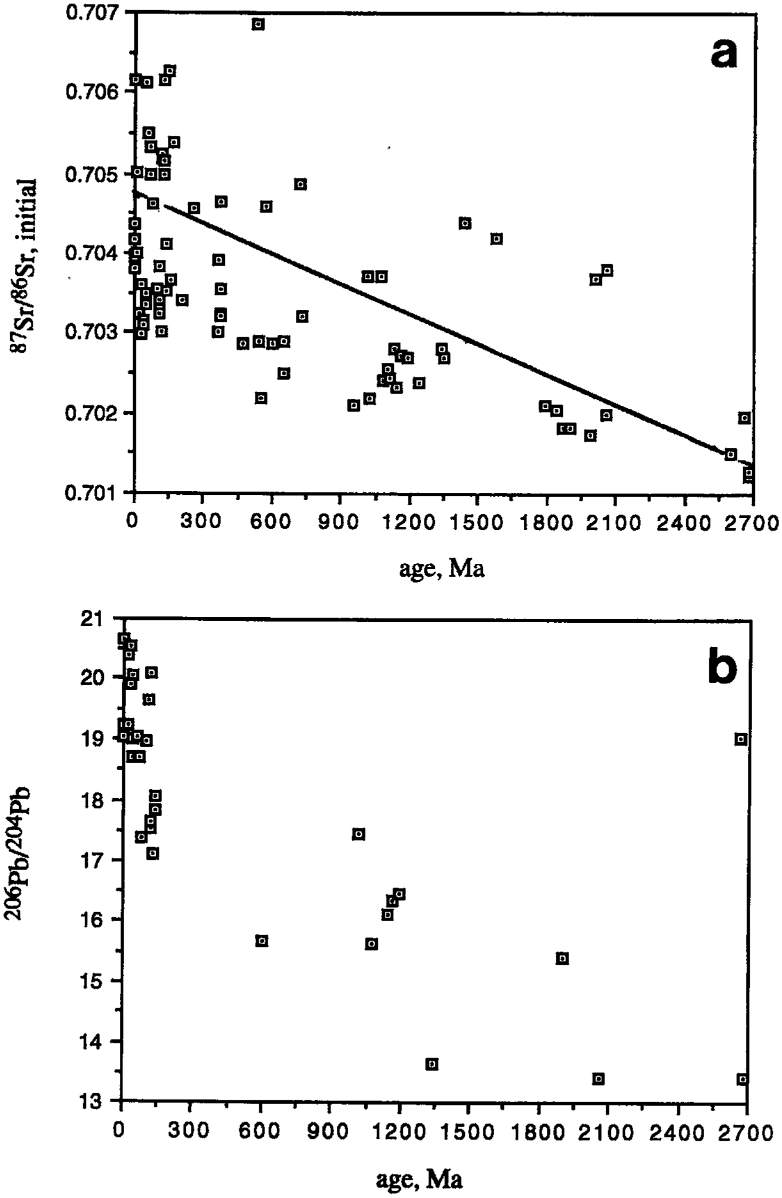

FIG. 2. (a) Initial $^{87}Sr/^{86}Sr$ *versus* age for 84 occurrences of carbonatites. Straight line is bulk-earth evolution line from Bell & Blenkinsop (1989, Fig. 12.1). (b) $^{206}Pb/^{204}Pb$ *versus* age for 33 occurrences of carbonatite.

Wyllie *et al.* 1990, Ringwood *et al.* 1992). The diversity of ratios at a given age reflects varying contributions from large volumes of source to small volumes of magma.

Carbonatite magmatism has occurred repeatedly over long time-spans in some regions. Examples include eastern Canada at 1900, 1100, 660–560, and 110 Ma (Bell & Blenkinsop 1989, Woolley 1989), West Greenland at 2650, 1300–1100, 600, and 176–169 Ma (Larsen & Rex 1992), East Africa at 1040, 750–680, 120–100, and 40–0 Ma (van Straaten 1989), and southern Africa at 2047, 1750, 750, 500, 200, 140–100, and 85–63 Ma (Harmer 1985, Woolley 1989, Ziegler 1992).

Some xenoliths of lithospheric mantle show the effects of metasomatism that occurred long before the xenoliths were entrained in the magma that carried them to the surface (Green & Wallace 1988, Hauri *et al.* 1993, Ionov *et al.* 1993, Rudnick *et al.* 1993, Smith 1979, Thibault *et al.* 1992). A few suites of xenocrysts and ultramafic xenoliths have provided documentation of multiple episodes in which carbon was introduced. Richardson *et al.* (1993) have identified three episodes of carbon influx and diamond generation beneath the Premier mine; one was from a strongly enriched harzburgitic source at 3200 Ma, a second was from a mildly enriched lherzolitic source at 1930 Ma, and the third was from a strongly depleted eclogitic source at 1150 Ma. Boyd *et al.* (1992) studied samples of "coated" diamond from Africa, Siberia, and Australia. The diamond coats are overgrowths precipitated from fluid that was fairly homogeneous in terms of carbon and nitrogen isotope ratios, and with $^{87}Sr/^{86}Sr$ ratios of 0.7038 to 0.7052, similar to sources of oceanic-island basalts. The core of these samples of coated diamond is older (to an unknown degree) and isotopically much more variable than the coats. Rudnick *et al.* (1993) inferred, from a study of mantle xenoliths from northern Tanzania, two episodes of carbonate metasomatism, one with less Ca and producing a different Nd isotopic ratio than the other. The significance of such recurrences was anticipated by Wyllie (1978, p. 442): "Repeated magmatic activity indicates that H_2O and CO_2 must be replenished, either from deeper sources or by recycling *via* subducted oceanic crust".

The recurrence of carbonatite magmatism in a specific region may not be due solely to replenishment of magma sources, however. Some carbonatite intrusive bodies are localized within linear grabens outboard of cratons, and especially at the intersections of faults (*e.g.*, Bailey 1993b, White *et al.* 1995). This distribution suggests that reactivation of fractures as conduits, in addition to replenishment of sources, is a cause of repeated and episodic emplacement of carbonatite in the crust.

Mantle xenoliths with metasomatic effects attributed to carbonatitic magma have been described from oceanic islands (*e.g.*, Hauri *et al.* 1993, Schiano *et al.* 1994), and carbonatites reported in oceanic crust are in the Canary and Cape Verde Islands (Le Bas 1984, Davies & Mendes 1991, Kogarko 1993) and on Trindade (Cornen *et al.* 1990). Furthermore, carbonatite associated with deep-water marine sediments occurs under the Semail ophiolite in the United Arab Emirates (Woolley *et al.* 1991). These occurrences suggest that carbonatites can occur on and within oceanic crust, but are usually buried or destroyed by subduction.

An old view, that carbonatites and their associated alkali-rich rocks are hallmarks of continental rifting, is being replaced by awareness that these rocks are not restricted to a single tectonic regime (Barker 1969, Woolley 1989, Bailey 1993b, Hall *et al.* 1995). They occur in oceanic and continental crust, and have formed in compressional fold belts and stable cratons as well as in regions of crustal extension. The widespread occurrence of xenoliths of carbonate-metasomatized lithospheric mantle suggests that, pending availability of heat for melting and an easy path to the surface, "carbonate magmatism is waiting to be unleashed" (Bailey 1993a).

HALTING THE RISE OF CARBONATITIC MAGMA

In addition to the factors that can stop the rise of any magma (heat loss, increase of solidus temperature with decrease in pressure, decrease in density and increase in strength of wallrock), carbonatitic magma can also be halted by reaction with wallrock (Dalton & Wood 1993a) to form calcium and magnesium silicates plus CO_2 as a component of a fluid phase (Table 4) and by less-oxidizing conditions that reduce carbonate to

TABLE 4. SOME PLAUSIBLE REACTIONS INVOLVING CARBONATES AND MANTLE SILICATES

$CaMg(CO_3)_2$	+	$4MgSiO_3$	=	$2Mg_2SiO_4$	+	$CaMgSi_2O_6$	+	$2CO_2$
dolomite	+	4 orthopyroxene	=	2 olivine	+	clinopyroxene	+	"fluid"
$3CaMg(CO_3)_2$	+	$CaMgSi_2O_6$	=	$2Mg_2SiO_4$	+	$4CaCO_3$	+	$2CO_2$
3 dolomite	+	clinopyroxene	=	2 olivine	+	4 calcite	+	"fluid"
$2MgCO_3$	+	$2MgSiO_3$	=	$2Mg_2SiO_4$	+	CO_2		
2 magnesite	+	2 orthopyroxene	=	2 olivine	+	"fluid"		
$2CaCO_3$	+	$2MgSiO_3$	=	$CaMg(CO_3)_2$	+	$CaMgSi_2O_6$		
2 calcite	+	2 orthopyroxene	=	dolomite	+	clinopyroxene		
$CaMg(CO_3)_2$	+	$2MgSiO_3$	=	$2MgCO_3$	+	$CaMgSi_2O_6$		
dolomite	+	2 orthopyroxene	=	2 magnesite	+	clinopyroxene		
$CaMg(CO_3)_2$	+	Mg_2SiO_4	=	$CaSiO_3$	+	MgO	+	$2MgCO_3$
dolomite	+	olivine	=	perovskite	+	periclase	+	2 magnesite

Analogous reactions involve carbonate–rich liquid, rather than calcite, dolomite, or magnesite.

elemental carbon (graphite or diamond) or to methane (Blundy *et al.* 1991, Ballhaus 1993). Both of these changes remove dissolved CO_3^{2-} from the magma, causing crystallization. The capacity of peridotites and pyroxenites to react with carbonatite magma is high; "... complete carbonatization of peridotite requires [addition of] 7 to 20 percent CO_2" (Schneider & Eggler 1986, p. 713), so that the buffering capacity of peridotite for carbonation reactions may be only locally reached.

Mantle redox reactions pertinent to carbonate stability are discussed by Ballhaus (1993), Blundy *et al.* (1991), Haggerty (1990), Kasting *et al.* (1993), Luth (1993), Luth *et al.* (1993), and Dalton & Wood (1995). In the upper lithospheric mantle, oxygen fugacity is apparently controlled by $Fe^{2+} - Fe^{3+}$ reactions (Ballhaus 1993), but at greater depths, reactions involving carbon probably become important. These include the enstatite + magnesite + olivine + graphite or diamond assemblage (Olafsson & Eggler 1983), which in $f(O_2)$ – temperature space extends from the quartz – fayalite – magnetite reaction to below the magnetite – wüstite equilibrium. On the other hand, according to Blundy *et al.* (1991), there is probably sufficient carbon (60 ppm C) in the upper mantle to control oxygen fugacity to within one log unit of the quartz – fayalite – magnetite "buffer". Luth (1993) concluded that the relative stabilities of elemental carbon and carbonate or CO_2 are influenced by varying assemblages of silicates; it is possible that, at the same pressure, temperature, and oxygen fugacity, peridotites can contain carbonate plus graphite or diamond, and eclogites can contain graphite or diamond without carbonate.

There may be portions of the lithospheric mantle in which oxygen fugacity is locally as low as the iron – wüstite buffer, at which CH_4–H_2O fluids would be stable relative to CO_2 fluid or carbonate liquid (Watson *et al.* 1990). Then, as recognized by Taylor & Green (1988), decreased fugacity of oxygen would result in increased temperature of the solidus and crystallization or decomposition of carbonate liquid. The other mechanism for halting the ascent of carbonate liquid, by reaction with silicates, seems more likely than reduction, because olivine and orthopyroxene, the two most abundant phases in most lithospheric mantle, are the dominant reactants in liberation of CO_2 from carbonate liquids (Table 4).

CONCLUSIONS

Carbonate-rich liquid should form at relatively low temperatures by partial fusion of carbonate-bearing mantle. If all the carbon in the mantle were juvenile, it is likely that the rate of carbonatite magmatism would have declined after peaking in the Archean. The distribution of ages of carbonatite emplacement (Woolley 1989, Veizer *et al.* 1992), however, shows no clear evidence of a secular decline in the rate of carbonatite magmatism. Unless the mantle is becoming increasingly oxidized, so that juvenile reduced carbon is being converted to carbonate, carbonatite magmatism must be sustained by carbon recycled by subduction.

The assumption that much of the carbon in carbonatites is recycled, not juvenile, leads to predictions that better agree with observations concerning the small volumes of individual bodies of carbonatite, the persistence, recurrence and widespread spatial distribution of carbonatite metasomatism in the mantle and magmatism in the crust, and the tendency for the sources of carbonatite magma to become more diverse and more radiogenic through time, through long-term storage in varied, small, and dispersed reservoirs. A single source of carbonatite magma appears unlikely. The return migration of deeply recycled carbon is probably slow, diffuse, and interrupted. Carbonatitic magmatism is like a poorly managed industry, at the mercy of erratic supplies of raw materials, inefficient processing, wasteful storage of the inventory, and fitful distribution of the finished product.

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APPENDIX: COMPILATION OF AGES AND ISOTOPIC RATIOS, CARBONATITES

Name	min age, Ma	min $^{87}Sr/^{86}Sr$	min $^{206}Pb/^{204}Pb$	reference
Alnö	553	0.7022		11
Amba Dongar	61	0.70549	19.05	43
Angico dos Dios	2011	0.7037		19
Anitapolis	129	0.70615	17.37	46
Araxa	83	0.70461	18.05	46
Bayan Obo	1580	0.70419		52
Big Beaver House	1109	0.70244		4
Borden	1872	0.70181	15.4	25
Bukusu	40	0.70315		5
Brava	3.7		19.01	26
Cargill	1900	0.70183	15.656	5
Catalao I	119	0.70520	17.51	9
Catalao II	119	0.70525	17.63	9
Chasweta	110	0.703836		53
Chilwa Island	136	0.7041		41
Chipman Lake	1029	0.7022		39
Clay–Howells	1072	0.70372		5
Dicker Willem	49	0.70336		37
Dolodau	2680	0.70122	13.41	44
Eisenberg	154	0.703669		53
Eureka	475	0.70286		47
Fen	539	0.702905	15.68	33
Firesand River	1087	0.70242	16.47	39
Fort Portal	0.004	0.70417		5
Fuerteventura	39		18.71	27
Gardiner Complex	50	0.7035		34
Goudini	1190	0.7027	17.46	33
Hogenakal	1990	0.70173		32
Homa Bay	13	0.70502		5
Ihouhaouene	1994	0.7094*		8
Iron Hill	570	0.7046		35
Iron Island	600	0.70287		4
Jacupiranga	131	0.70500	17.10	46
Juquia	133	0.70515		2
Kaiserstuhl	17	0.70360	19.24	40
Kaluwe	110	0.703286		53
Kangankunde	123	0.703016	20.11	53
Kerimasi	0.5	0.703967	20.664	36
Khibina VIII	366	0.703924		23
Kovdor	370	0.703233		24
Kruidfontein	1246	0.7024		13
Lac Shortt	2680	0.70129	13.41	44
Lackner Lake	1138	0.70282		3
Lages	70	0.7050		19
Little Murun	145	0.70626		31
Magnet Cove	97	0.70355	18.98	25
Mount Weld	2060	0.7020		30
Mountain Pass	1440	0.7044		51
Mud Tank	732	0.7032		16
Nachendazwaya	655	0.7025	42.00*	33
Napak	20	0.70323	20.40	42
Nemegosenda	1015	0.70371	16.36	25
Newania	959	0.7021		48
Oka	110	0.70323	19.65	45
Oldoinyo Lengai	0	0.70437	19.24	6
Ozernaya Varaka	376	0.703534		24
Panda Hill	113	0.703407		53
Phalaborwa	2060	0.70379	19.03	38
Prairie Lake	1165	0.70273	16.13	39
Radian Ridge	531	0.70687		20
Rocky Boy	45	0.70611		17
Rusukere	0	0.70417		5
Santiago	8.5	0.7040		12
Schryburt Lake	1140	0.70234		4
Seabrook Lake	1103	0.70256		4
Sevathur	720	0.70489		50
Shawa	209	0.7034		28
Shombole	2	0.70395		7
Siilinjarvi	2605	0.70151	13.65	44
Singertat	2664	0.701975		10
Sökli	367	0.703016		24
Spanish River	1838	0.70205		4
Spitskop	1341	0.7028		22
St–Honoré	650	0.70289		4
Stukpan	1354	0.7027		47
Sukulu	40	0.70310	20.07	33
Suswa	0.24	0.706144		29
Tadhak	254	0.70457	18.712	49
Tamazert	44		18.57	21
Tapira	70	0.70532	17.83	46
Tchivira–Bonga	135	0.70353		14
Tororo	32	0.70360	20.56	33
Trindade	< 3.7	0.70379	19.04	15
Turiy Mys	373	0.703197		24
Venturi Township	1790	0.7021		18
Vuorijarvi	370	0.704658		24
Walloway	170	0.7054		33
Westland	25	0.70299	19.90	1

* aberrant values not included in Figures 1 and 2. Where more than one value is published, the lowest was selected for age, initial $^{87}Sr/^{86}Sr$, and $^{206}Pb/^{204}Pb$. Only one reference is listed for each occurrence, and this one may not be the source of all listed data, but should serve as a guide to other publications.

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